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To Mr. F.J. Kee
Director of Research

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TRANSFORMER GAS ANALYSIS

R.E. Massey

A vacuum extraction/gas chromatographic technique for the analysis of dissolved gases in transformer oil has been developed and is being used on a routine basis in the Analytic Services Section. An existing vacuum system has been modified and interfaced with a modern microprocessor controlled gas chromatograph. The sample throughput with this system is 12 to 15 samples per day, the cost/analysis has been significantly reduced, and the analytical data is more reliable. The method has been documented and is recommended for routine transformer gas analyses.

1.0 INTRODUCTION

The detection of certain gases generated in oil-filled transformers is frequently the first available indication of a malfunction that may eventually lead to failure. New transformer oils contain very little dissolved gas but during normal operation of the transformer some gases are formed and O_2, N_2 and CO_2 dissolve due to exposure of the oil to air. When faults such as arcing, corona discharge, low energy sparking, severe overloading and overheating in the insulating materials occur in the transformer, the oil and/or insulation material decomposes. The type of fault may be determined by the kinds of gases generated. The extent of the fault may be determined by the rate of generation of gases with time. Severe faults are usually detected in the field and then confirmed by gas analysis. Incipient faults are detected with the comparison of operational and gas analysis data collected over time (a sampling periodicity of one year is normal).

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The individual component gases that may be identified and determined include:

Hydrogen	H_2
Oxygen	O_2
Nitrogen	N_2
Methane	CH_4
Carbon Monoxide	CO
Carbon Dioxide	CO_2
Ethylene	C_2H_4
Ethane	C_2H_6
Acetylene	C_2H_2
Propylene	C_3H_6
Propane	C_3H_8
Butane	C_4H_{10}

The sampling and analysis of transformer oils and the interpretation of the data is a subject which has been covered thoroughly in the literature. The key references are listed below.

The International Electrotechnical Commission (IEC)/1,2/
The American National Standards Institute, Inc. (ANSI)
The Institution of Electrical and Electronics Engineers, Inc. (IEEE)/3/
The American Society of Testing Materials (ASTM)/4,5/.

At Ontario Hydro the Transmission Stations Department of Thermal and Hydraulic Generation Division have established a sampling program for approximately 10 000 transformers. The Analytic Services Section at OHRD have provided transformer gas analysis since 1971. Over the past two years a great deal of effort has been directed towards improvements in the capacity, reliability, and cost of transformer gas analysis. In addition we have attempted to develop an understanding of the important aspects in the sampling and storage of oil samples which has not been adequately addressed in the past.

This report describes the changes in the analytical hardware which have improved the performance over the previous gas analysis system. These include: the application of a state-of-the-art gas chromatograph; the modification and interfacing of a vacuum extraction apparatus to the gas chromatograph; and the development and documentation of standard methods of sample handling and analysis. Various aspects of sampling and storage were studied and these will be reported.

2.0 ANALYTICAL CHEMISTRY

2.1 Sample Collection and Storage

Although there are three types of containers suitable for the collection and storage of transformer oils, Ontario Hydro and most other utilities have selected gas-tight glass syringes fitted with nylon-teflon three-way valves. To sample a transformer the syringe is connected to the transformer sampling port with a short piece of gas-impermeable and oil resistant plastic or rubber tubing. The three-way valve and syringe piston are manipulated to take the sample. Care must be taken at this point to ensure that all atmospheric gases are excluded, the sample is representative and is not partially de-gassed. Ontario Hydro has a standard procedure for the syringe sampling of transformer oils/6/.

When the sampling process is complete, the syringe valve is closed to prevent ingress of atmospheric gases, and the syringe is packed in a cardboard box. The box provides an adequate shipping container while preventing the exposure of the oil to damaging ultraviolet light.

Syringes are considered to be suitable for sample storage if less than 2.5% of the hydrogen is lost in one week. Assuming 5% in the precision of the analytical method and a loss of 2.5%/week, a significant difference in the gas concentration could only be measured after two weeks. The syringes used by Ontario Hydro easily meet the leak rate criterion.

2.2 Vacuum Extraction of Dissolved Oil

A vacuum system is used to receive a subsample of the oil, to efficiently remove the dissolved gas from the oil, and to compress the extracted gas so that an aliquot may be taken for the gas chromatograph. A schematic diagram of a vacuum system is shown in Figure 1.

The efficiency of gas extraction from oil depends upon thermodynamic factors, such as the volume of sample and vacuum system and the solubility of gas in oil. The rate of gas evolution from the oil into the evacuated space is determined by kinetic factors (the viscosity of the oil, the diffusion rate of gas through the oil, and the effective surface area of the sample).

The solubilities of gases in transformer oils have been measured at 760 mm Hg and 25°C.

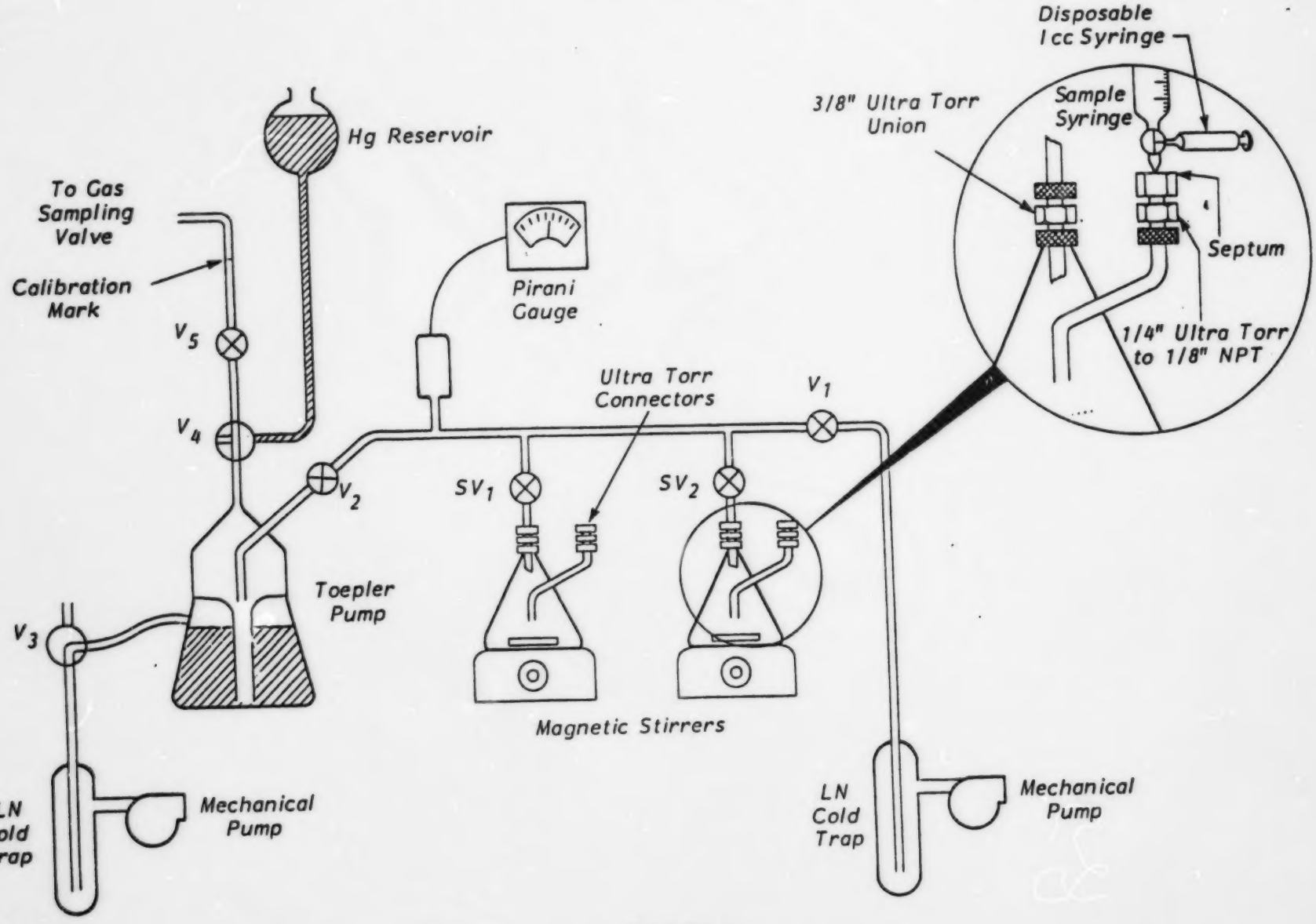

FIGURE 1

THE VACUUM SYSTEM

Gas	Solubility (μL/L)
Hydrogen (H_2)	56 000
Nitrogen (N_2)	97 000
Air	103 000
Carbon Monoxide (CO)	133 000
Argon (Ar)	150 000
Oxygen (O_2)	179 000
Methane (CH_4)	438 000
Carbon Dioxide (CO_2)	1 170 000
Acetylene (C_2H_2)	1 220 000
Ethylene (C_2H_4)	1 760 000
Ethane (C_2H_6)	2 590 000
Propylene (C_3H_6)	12 000 000
Propane (C_3H_8)	11 000 000
Butane (C_4H_{10})	20 000 000

The extent to which a particular gas is extracted from the oil in a vacuum system can be calculated using the following equation:

$$Ei = \frac{1}{1 + \frac{Ki * Vo}{Vt - Vo}}$$

where;

Ei = Degassing coefficient of gas component i

$$= \frac{\text{amount of i in gas phase}}{\text{amount of i remaining in the oil}}$$

Vo = Volume of the oil sample

Vt = Total internal volume of vacuum system

Ki = Ostwald solubility coefficient of component i
= solubility x 1 000 000

A typical vacuum system has a total volume of between 500 and 2 000 mL. Using Vt = 1 000 mL, the efficiency of extraction can be calculated for various gases and oil sample sizes. Some examples are shown in Table 1.

TABLE 1

EXTRACTION EFFICIENCY AND OIL VOLUME

Gas	% Efficiency	
	5.00 mL of Oil	200.0 mL of Oil
H_2	99.97	98.62
CO_2	99.42	77.37
C_2H_6	98.72	60.70
C_4H_{10}	90.88	16.67

Quantitative extraction is favoured by a small oil sample volume relative to the total volume of the vacuum extraction apparatus. Using 5 mL of oil, no correction for extraction efficiency is required. Larger samples require an additional correction factor but provide more gas for analysis and lower detection limits.

The rate of degassing of a relatively viscous oil is slow and is determined by the very low diffusion rates of gas through the oil. Most vacuum extraction systems include magnetic stirrers and fritted glass tubes through which the sample is passed as it enters the vacuum apparatus. These devices ensure that all the dissolved gas is removed from the oil in a reasonable time (2-10 min).

2.3 Gas Chromatography of Extracted Gases

In the present gas chromatograph the elemental gases H_2, O_2 and N_2 are detected by a thermal conductivity detector using argon as carrier. Argon carrier provides the best possible detectability of hydrogen with adequate detectability of oxygen and nitrogen.

Hydrocarbons are detected by a flame ionization detector as well as the carbon oxides which are converted to methane by means of a nickel catalyst. Detection of CO_2 and CO in this manner allows column temperature programming during the chromatographic run minimizing the analysis time.

Two columns are needed for the complete separation: a molecular sieve column for H_2, O_2, N_2, CH_4 and CO; and a porous polymer column for CO_2, C_2H_4, C_2H_6 and C_2H_2. The two columns are connected in a series/by-pass configuration and the valve and detector switching is performed automatically by the microprocessor unit in the instrument.

The chromatographic signal is sent to a data processor which measures the area of chromatographic peaks, identifies the peaks according to their retention times, compares the areas to those of standards, calculates each component concentration and presents these in a report.

A comparison of new and old transformer dissolved gas analytical technology is presented in Appendix I.

3.0 EXPERIMENTAL

3.1 Instrumentation

A Varian 6000 Series microprocessor controlled gas chromatograph and a Vista 402 data station were used for this work. Six- and eight-port zero dead volume gas sampling valves were installed in a modified injector block and a 1/8 in x 5.5 ft stainless steel column packed with Molecular Sieve 13X, 45/60 mesh and a 1/8 in x 12 ft stainless steel column packed with Poropak N, 50/80 mesh were installed in a series/bypass configuration. In the other injector port a 1/8 in x 8 in stainless steel column packed with Ni on Chromosorb W was installed and operated at 375°C. Thermal conductivity and flame ionization detectors were mounted in series. The data system included a single floppy disc drive for raw data storage and a printer/plotter for permanent records of data and chromatograms.

An existing vacuum extraction system was modified for use with the gas chromatograph. The vacuum system had a total volume of approximately 800 mL and included a Toepler pump, twin gas burets, a Hg manometer for total gas measurement, and a septum for gas sampling. Two mechanical vacuum pumps were used, one for the operation of the Toepler pump and the other for the main vacuum system. The gas burets and sampling septum were removed and the Toepler pump connected directly to the gas sampling valve of the gas chromatograph. Two sample extraction flasks were installed to increase the throughput of samples and all ground glass joints were replaced with Ultra-Torr connectors and any unnecessary glass valves removed.

To simplify gas analysis, it was proposed that the determination of the total gas content of oils be made by summing all data for component gases as measured by the gas chromatograph. A number

of real transformer oils were extracted and the total gas measured by differential pressure measurement in a gas buret and by the method described above.

Expected ranges of dissolved gases in transformer oils were characterized by preparing histograms for 100 transformers selected at random. From these data an optimum gas mixture was chosen which would correspond to a typical gas extract. Two primary standard gas mixtures were acquired from a local supplier and these were in turn used to evaluate the linear ranges of the gas chromatograph, to determine the optimum sample size to be extracted, and to estimate the detection limits of the test.

The final procedure for the analysis was documented and delivered to the laboratory for discussion and revision and a final version of the standard test method prepared.

The results of a recent ASTM round robin transformer oil study were examined and the precision of other laboratories compared with that obtained in this work.

3.2 Modifications to the Valving System

Most transformer oils contain heavier molecular weight hydrocarbon gases such as propane, butane, and pentane which are extracted from the oil. Since the client did not require analysis of these species and chromatographic time required to elute these heavier hydrocarbons decreased the availability of the system, the gas chromatograph was reconfigured to allow the heavier hydrocarbons to be vented from the column system. The original 6-port zero dead volume gas sampling valve was replaced with a 10-port valve, a 1 ft x 1/8 in Poropak N 50/80 mesh column was placed in series with the original column, and an extra flow regulating valve added to provide backflush gas for the precolumn.

3.3 Study of the Sampling and Storage of Low Oxygen-Containing Oils

During initial stages of the development work it was observed that in some field samples the oil was not homogeneous with respect to oxygen and the measured O_2 content would decrease as sub-samples were taken from the sample syringes. A modest investigation was carried out to study this problem. A large volume of new transformer oil was sparged with N_2 for 48 hours and then sampled into clean syringes. A sub-sample of the oil was analyzed immediately and the syringes were then stored for 45 days and analyzed periodically. In addition to these samples one transformer selected by Thermal and Hydraulic Generation

Division was sampled from the bottom and the top. The data obtained from these analyses was used to determine whether gas concentration gradients existed in a large oil-filled transformer.

3.4 Introduction of a Quality Assurance Sample

A standard quality assurance practice in the analytical laboratory is to analyze a well characterized sample along with unknowns. Due to difficulties in preparing synthetic gas in oil samples, a decision was made to use the oil from an operating transformer. The particular transformer chosen was T13 at Manby TS as this unit contained typical and stable gas concentrations. As a routine, this standard sample was analyzed daily and the results archived.

4.0 RESULTS AND DISCUSSION

4.1 Dissolved Gas Concentrations and Calibration Ranges

Dissolved gas in oil data for 100 transformers were collected and histograms for each gas component plotted. Two separate distributions for each gas were evident; a lower gas content for typical transformers and a high gas content for older transformers or ones experiencing some type of fault. The approximate ranges of dissolved gases for typical and faulted oils are shown in Table 2.

TABLE 2

GAS IN OIL RANGES FOR TYPICAL AND FAULTED OILS

Gas	Gas Concentration Range (µL/L)	
	Typical Oils	Faulted Oils
H_2	5-8 00	50-6 000
O_2	300-25 000	300-25 000
N_2	17 000-90 000	17 000-90 000
CH_4	8-280	200-35 000
CO	80-1 000	20-2 000
CO_2	200-4 000	1 000-10 000
C_2H_4	1-1 000	500-85 000
C_2H_6	2-200	500-18 000
C_2H_2	2-300	2-34 000

Due to the large concentration differences between typical and faulted oil samples, it was not possible to apply one standard procedure to both sample types. Therefore two different methods were required, one called TRANS for typical oils and the other called TRANS HI for faulted samples. The two methods differ in the amount of oil used for analysis, the degree of compression of the extracted gas, the calibration standard used and the detector sensitivity. The applicable concentration range of methods TRANS and TRANS HI and the concentration of each gas component in the calibration standard purchased is listed in Table 3.

TABLE 3

METHOD RANGES

Gas	Gas Content (µL/L)			
	Typical Oils	Primary Standard	Faulted Oils	Primary Standard
H_2	5-600	1 492	125-15 000	14 900
O_2	100-40 000	199 100	250-100 000	30 300
N_2	100-150 000	769 572	250-375 000	551 000
CH_4	5-100	497	50-25 000	49 600
CO	20-1 200	5 960	500-7 000	14 900
CO_2	20-4 000	19 900	500-15 000	40 100
C_2H_4	2-200	497	50-20 000	49 700
C_2H_6	2-200	497	50-17 500	49 500
C_2H_2	2-200	497	50-5 000	9 940

4.2 Response Curves for Transformer Gases

The detector responses as a function of concentration for all gases of interest are shown in Figures 2 and 3. For both the methods TRANS and TRANS HI the response is rectilinear and the calibration curves pass through the origin.

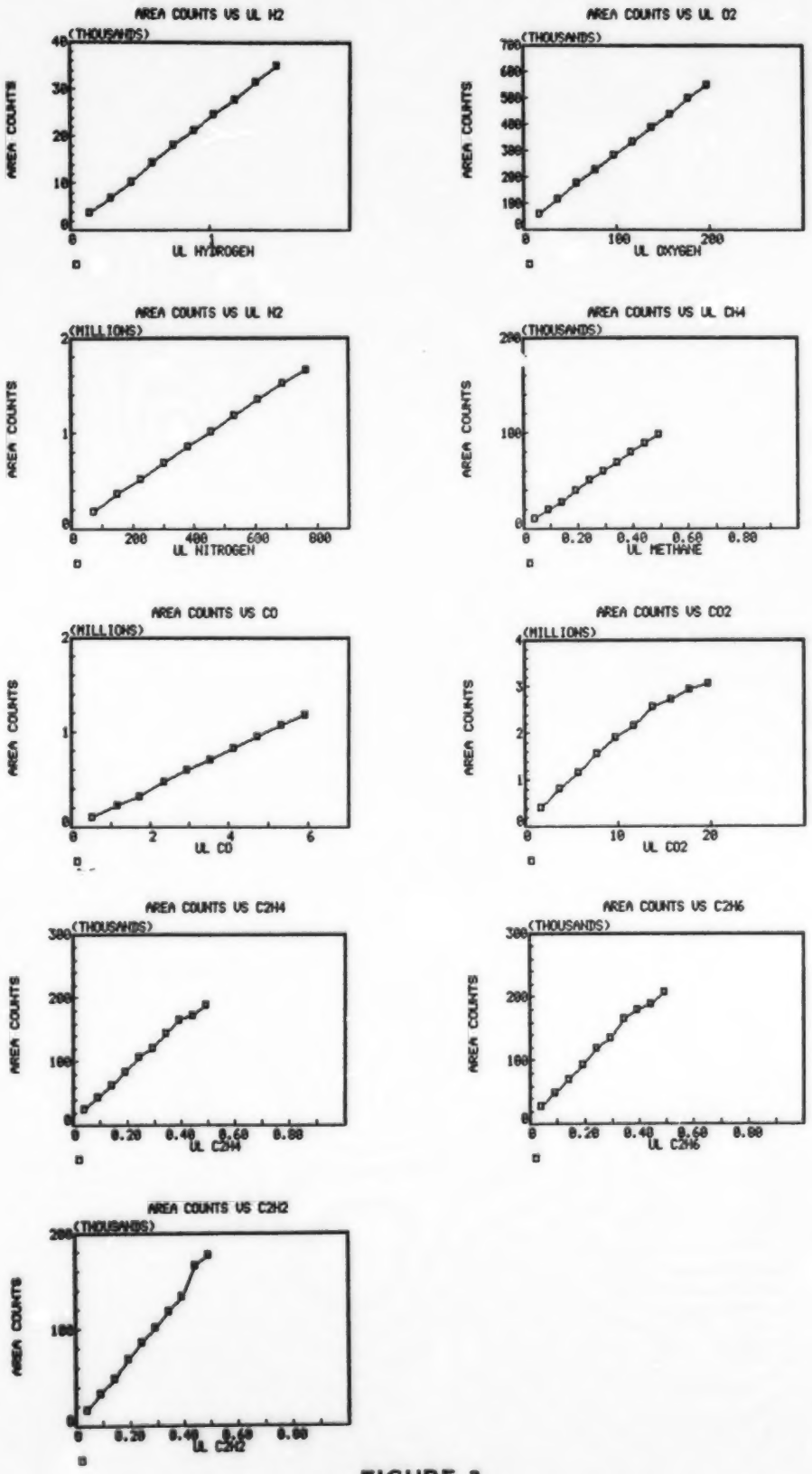

FIGURE 2

CALIBRATION CURVES FOR 'TRANS' STANDARD

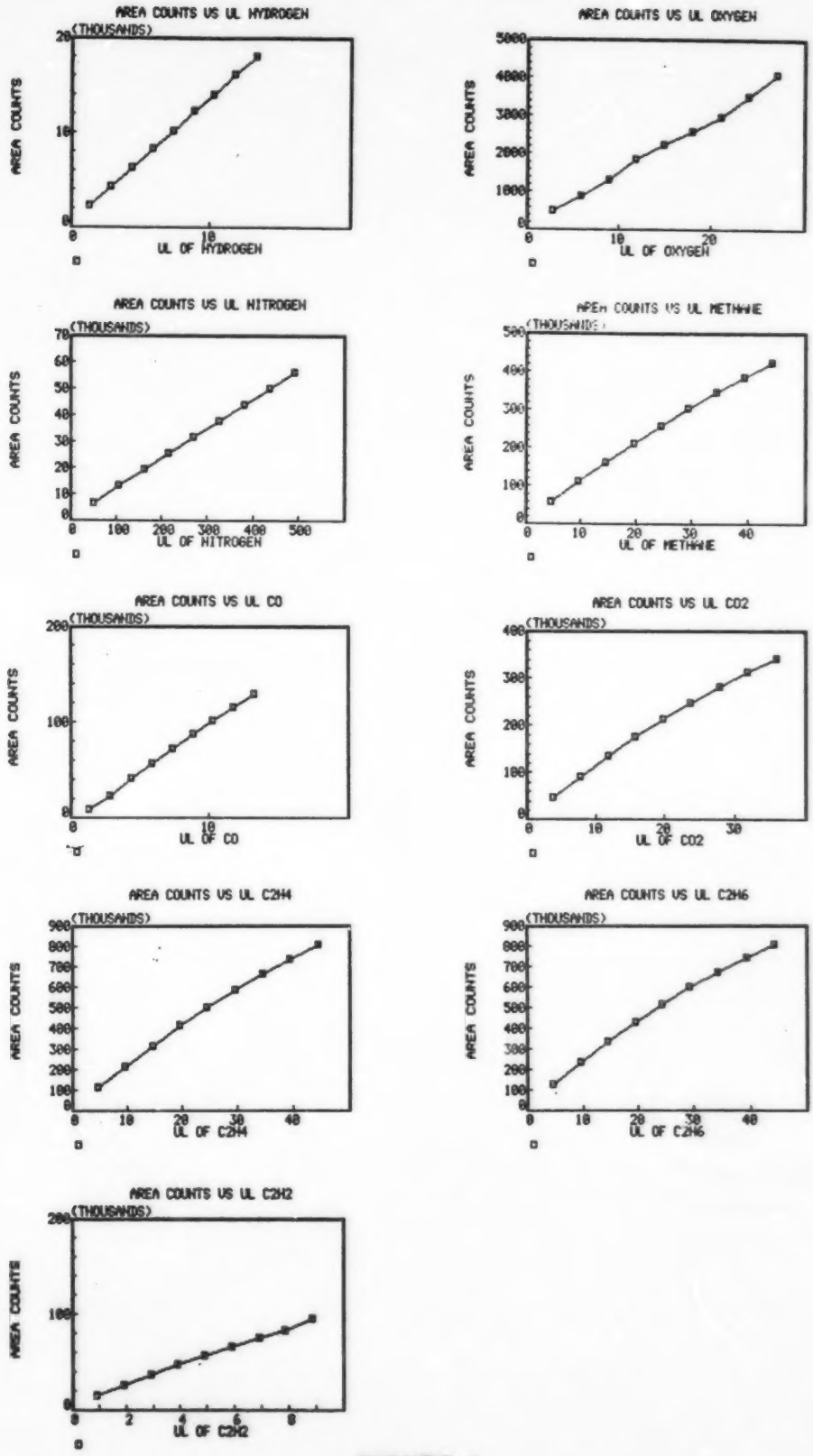

FIGURE 3

CALIBRATION CURVES FOR 'TRANS HI' STANDARD AND FAULTED OIL

166972 RD

4.3 Total Gas Measurement

The total dissolved gas content was measured in a number of transformer oil samples with a gas buret and with the gas chromatograph, by summing the measured concentrations of all component gases. These data are presented in Table 4.

TABLE 4

COMPARISON OF GAS BURET AND GC MEASUREMENT OF TOTAL EXTRACTED GAS

Sample	Total Gas Measurement (mL/L)	
	GC Measurement	Gas Buret
1	90	97
2	64	64
3	55	62
4	47	48
5	46	48
6	98	99
7	83	91
8	90	92
9	86	93
10	77	80
11	78	83

These data indicate that within experimental error the gas chromatographic measurement is equivalent to the gas buret measurement. It is expected that the buret measurements would be higher due to the possibility of air leakage through the sampling septum. The use of the former greatly simplifies the test and the requirements of the vacuum system.

4.4 Precision

The precision of the transformer gas analysis system was measured by making repetitive measurements of the QA sample. Six 30 mL syringes were filled with the oil at Manby TS each month and the contents analyzed over a 30 day period. Initially a 5 mL subsample from each syringe was analyzed and the in-run precision computed. A 5 mL portion was then analyzed each day over a period of 30 days and the data obtained used to compute the day-to-day precision. The data is summarized in Table 5.

The average good lab precision is that of a number of laboratories who participated in a recent round robin survey. This data is derived in Appendix II. The precision obtained by the system described here is at least as good as that obtained in the ASTM survey. The day-to-day precision is higher than the in-run as expected.

TABLE 5

COMPARISON OF ASTM AND OHRD PRECISIONS

Gas	Avg Good Lab	OHRD In-run	OHRD Day-Day	QA Level µL/L
H_2	10.6	4.6	4.9	45
O_2	12.6	2.4	0.4	25 000
N_2	7.6	0.9	3.8	67 000
CO	6.2	2.0	4.5	20
CO_2	6.6	2.7	2.6	300
CH_4	5.0	0.9	3.2	2 400
C_2H_6	9.0	2.3	6.6	35
C_2H_4	5.2	2.1	6.8	11
C_2H_2	4.8	3.5	5.4	55

4.5 Modifications to the GC Valving System

The valving of the gas chromatograph was modified by removing an existing 6-port gas sampling valve and installing a 10-port valve and short Poropak precolumn. The length of the precolumn was optimized to allow the backflush of the precolumn to be initiated after N_2 elution in the chromatogram. As a result of this modification the run time was reduced from 25 minutes to 12 minutes which significantly increased the sample throughput per day. Typical chromatograms before and after the modification are shown in Figure 4.

4.6 Sampling and Storage of Oil Samples

The observation that some transformer oil samples containing less than saturation amounts of air were not homogeneous with respect to O_2, led to a modest investigation. The possible causes were subdivided into three categories; analysis, sampling and sample integrity.

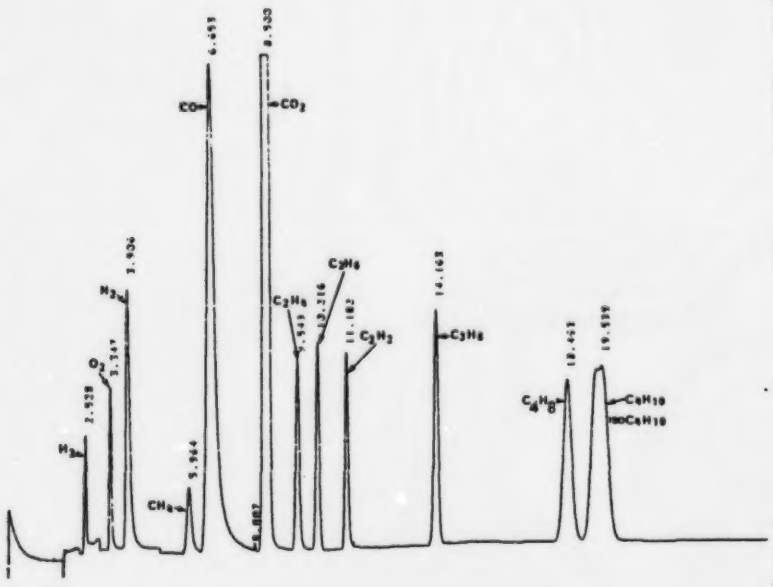

FIGURE 4A

CHROMATOGRAM OF TRANS STANDARD WITHOUT PRECOLUMN BACKFLUSH TO VENT

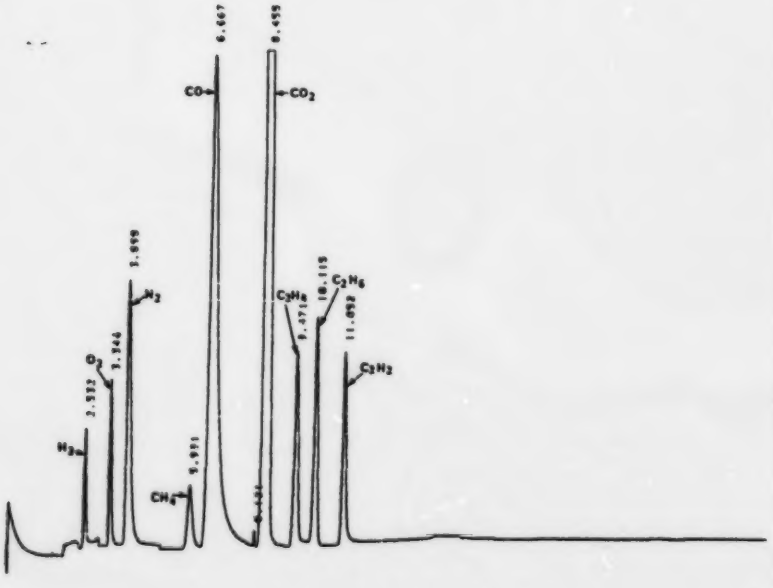

FIGURE 4B

CHROMATOGRAM OF TRANS STANDARD WITH PRECOLUMN BACKFLUSH TO VENT

4.6.1 Analysis

The two main concerns are the efficiency of O_2 removal from oil and the loss of sample integrity during the transfer of a subsample of oil from the syringe to the vacuum system. Since oxygen is one of the least soluble gases it should be extracted from the oil with virtually 100% efficiency. To prove that the procedure for taking a subsample is correct, one syringe of transformer oil was analyzed five times in succession and the analytical data examined (see Table 6).

TABLE 6

REPETITIVE ANALYSIS OF AN OIL SAMPLE

Gas	Gas Concentration (μL/L)				
	Sub-Sample				
	1st	2nd	3rd	4th	5th
H_2	56.1	59.6	60.8	55.9	59.5
O_2	25 900	25 540	24 830	24 550	23 790
N_2	65 000	65 900	65 550	65 720	65 340
CH_4	24.7	25.0	24.9	24.5	24.5
CO	319.2	329.8	325.5	321.1	325.2
CO_2	1 336	1 354	1 321	1 469	-
C_2H_4	45.6	46.9	46.2	45.2	45.6
C_2H_6	13.02	13.48	13.13	13.04	13.24
C_2H_2	57.5	54.8	55.3	57.1	
Vol%	9.31	9.44	9.30	9.28	9.18

During the short time when oil is being transferred to the vacuum system the bulk of the oil is exposed to a vacuum and if the diffusion rate of gas through the oil is fast enough the unsampled oil could be depleted in gas. The data indicate that the sample introduction technique does not alter the concentration in the bulk oil sample.

4.6.2 Sampling

The major aspects to be considered in the sampling process are the homogeneity of the oil, whether the sample is representative, and whether the sampling equipment is adequate.

The homogeneity of an oil with respect to dissolved gases is dependent upon the rates of mixing of the oil and the rate of generation of fault gases. A typical transformer was selected and samples were drawn at the top of the transformer (gas relay) and from the bottom (normal sampling point). The data for the two samples are shown in Table 7.

TABLE 7

TRANSFORMER OIL HOMOGENEITY

Gas	Gas Content (µL/L	
	Top (Gas Relay)	Bottom
H_2	72	72
O_2	25 200	24 600
N_2	70 800	66 800
CH_4	29	28
CO	356	338
CO_2	2 700	2 650
C_2H_4	66	64
C_2H_6	14	13
C_2H_2	88	80

No significant differences were found in the two samples indicating that the oil in the transformer was homogeneous.

The method of preparation of the glass syringes used for sampling was found to be of critical importance in the sampling of low O_2-containing oils. This was discovered during the set-up of an oil storage study in which a number of syringes were filled with N_2-sparged oil. The data for two syringes is presented in Table 8.

TABLE 8

SAMPLING AND STORAGE OF LOW O_2 OIL

Storage Time (Days)	Gas Content (µL/L)			
	Sample No. 1		Sample No. 2	
	O_2	N_2	O_2	N_2
0	8 200	124 700	1 050	92 200
15	367	86 800	510	86 100
45	350	90 900	330	91 300
45	390	90 000	380	87 900
45	380	88 400	300	92 600

The original O_2 and N_2 contents of the oil are 350 and 90 000 µL/L, respectively and the high values obtained initially are the result of air contamination by the syringe during sampling. The glass surfaces of the syringes had been cleaned with a solvent and dried and as a result they were difficult to wet with the oil. The glass surface entrained minute air bubbles which agglomerated on standing and the larger bubbles migrated to the top of the oil. Since the two syringes were stored with the syringe tip up, high O_2 and N_2 readings were obtained in the first subsample. In time air bubbles will dissolve, but due to the low diffusion rate of gas through oil, localized high concentrations of O_2 and N_2 will be formed.

The magnitude of air entrainment is highly dependent upon the condition of the glass surface of the syringe. Instead of cleaning and drying the syringes all syringes leaving our laboratory are now drained and purged with new oil. This technique assures a wetted surface and minimizes air entrainment.

4.6.3 Sample Integrity

The integrity of a sample can be lost by diffusion of gases in and out of the syringes and by photochemical reactions. No significant changes in the gas content of oil stored in syringes for periods of up to 45 days have been observed. This is true for the low gas containing oils studied in Section 4.6.2 as well as the QA sample which is routinely stored for 30 day periods.

When oils are exposed to ultraviolet light, O_2 reacts with components of the transformer oil to form CO_2. This reaction was demonstrated in an accelerated exposure test/7/.

Gas \ Exposure Time (Days)	Gas Content (µL/L			
	0	9 days	45 days	90 days
O_2	30 500	25 400	2 600	330
CO_2	690	950	780	1 200

Oxidation of oil is delayed by the exclusion of light from the sample. If oxidation does occur it is highly unlikely that zones of differing concentration would be formed.

The apparent inhomogeneity of oil samples with respect to O_2 in low O_2-containing oils has been attributed to the contamination of the oil with air during sampling and steps have been taken to avoid this problem.

4.7 Quality Assurance Sample

To aid the analyst in maintaining a consistent level of quality, an oil sample with a well established gas content was selected and has been analyzed with every batch of samples. The oil was obtained from an operating 227 000 L oil-filled transformer which contained both typical amounts of dissolved gases and gas contents which had remained relatively constant with time. A Manby TS transformer met both of the above requirements. The analytical data obtained for numerous samples of this oil collected during the period of January 1983 to January 1984 are plotted in Figure 6. The variations in the concentrations of the gas components with time were found to be small enough to make the sample useful as a quality assurance sample.

As a routine, six syringes were filled with oil at one time which provided enough sample for at least 20 separate working days. It has been found that the gas content in the oil stored in glass syringes remains constant for at least 30 days when the sample is stored away from light. This makes the acquisition of the sample much simpler.

An analysis of the quality assurance sample is carried out with every batch of unknown samples. This practice has proven useful in establishing the precision of analysis, in identifying specific instrument problems, and in the provision of high quality data.

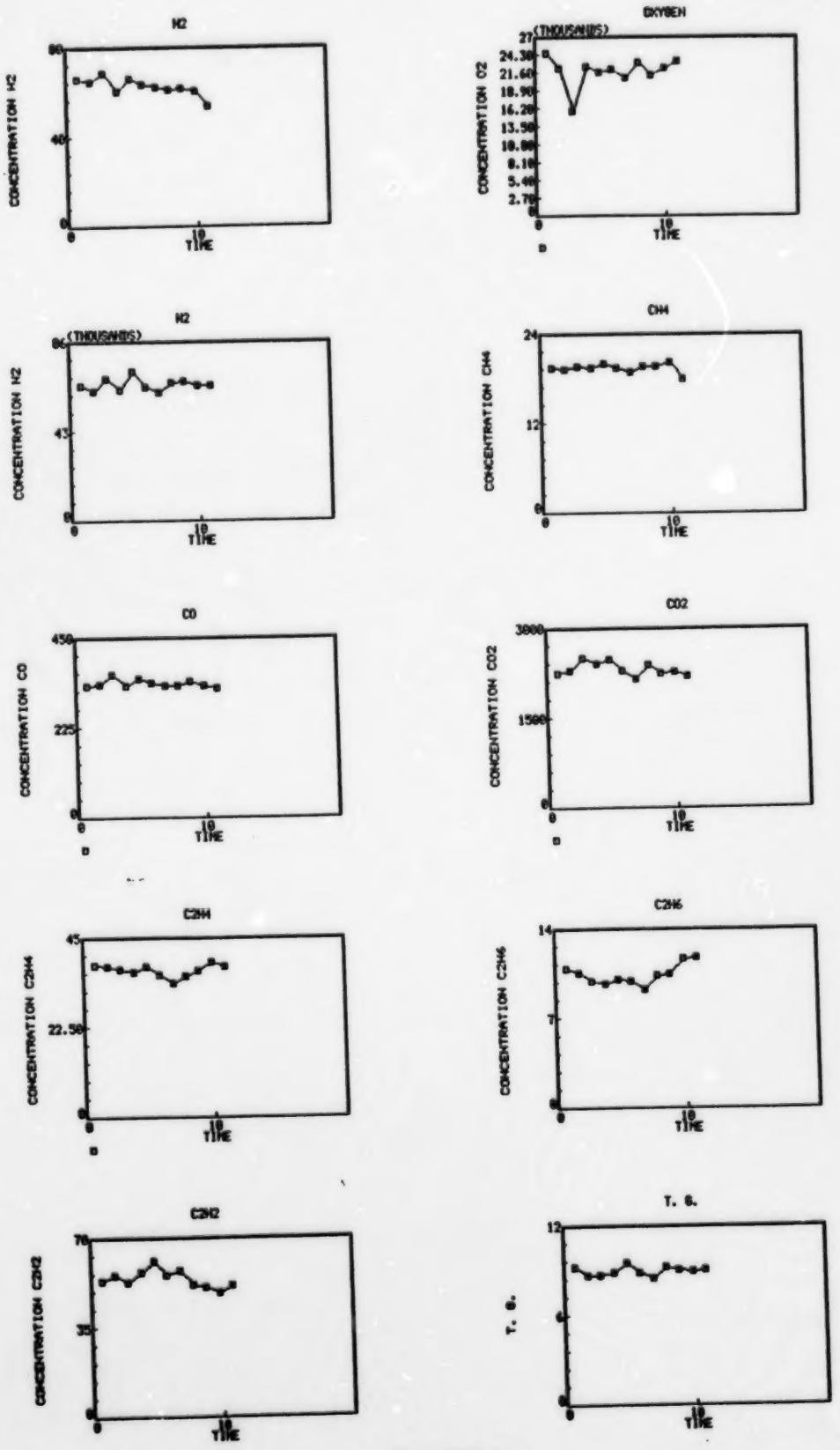

FIGURE 5

STABILITY OF INDIVIDUAL GASES IN THE Q.A. SAMPLE

5.0 CONCLUSIONS

An improved procedure for the determination of dissolved gas in transformer oil has been developed which provides a simpler, more reliable, and cost effective analysis. The analysis system includes a new gas chromatograph, a redesigned vacuum system, and a data processing unit. Standard procedures for the analysis have been documented and recommended for routine use in the Analytic Services Section.

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APPENDIX I

COMPARISON OF ANALYTICAL METHODOLOGY

Transformer gases are best separated on two chromatographic columns. H_2, O_2, N_2, CH_4 and CO are separated on Molecular Sieves and CO_2, C_2H_2, C_2H_4, C_2H_6 and heavier hydrocarbons on porous polymers. Both columns can be installed in the gas chromatograph and operated at the same column temperature. With the optimum temperature and carrier gas flow conditions, a chromatographic run can last from 10 -15 min but due to the presence of higher molecular weight hydrocarbons which can elute up to one hour after injection, the chromatograph may not be available for long periods of time.

The detectors which are most applicable to transformer gas analysis are the Thermal Conductivity Detector (TCD) for the permanent gases and the Flame Ionization Detector (FID) for the hydrocarbon gases. This choice is based on known gas concentrations, required detection limits and required detector linear ranges. Helium Ionization Detectors (He) have also been applied, but the earlier models of these were limited by a narrow linear range, the need for constant maintenance, and the instability of the detector to changes in the column temperature. Some of the most important attributes of all three detectors are listed in Table I-1 and these must be compared to the typical concentrations of gases in transformer oils listed in Table I-2.

TABLE I-1

TGA DETECTORS

Detector	Linear Range	Detection Limit	Temperature Program
TCD	0-100%	1 nL H_2	no
FID	10^7	0.1 nL C	yes
He	10^2	0.005 nL O_2	no

TABLE I-2

CONCENTRATION RANGE OF DISSOLVED GASES

Gas	Gas Concentration Range (μL/L)	GC Injection Vol (nL)
H_2	5-6 000	25-30 000
O_2	300-25 000	1 500-125 000
N_2	17 000-90 000	8 500-450 000
CH_4	8-35 000	40-175 000
CO	80-2 000	400-10 000
CO_2	200-10 000	1 000-50 000
C_2H_4	1-85 000	5-425 000
C_2H_6	2-18 000	10-90 000
C_2H_2	2-34 000	10-170 000

Although the helium ionization detector is very sensitive, it is not well suited to transformer gas analysis due to the limited linear range. On the other hand the TCD and FID detectors are well suited to the application.

In the past a syringe was used to sample a gas from the vacuum system and inject into the gas chromatograph. This technique required a gas buret fitted with a septa for syringe sampling of the extracted gas. Experience has shown that contamination of the sample from atmospheric air is a real problem since septa leak and removal of all residual air from the needle tip of the syringe is not possible. High quality gas sampling valves are now available which can be directly incorporated into the vacuum system. These provide a direct interface between the vacuum system and gas chromatograph, are leak-free, and provide higher precision.

Recently commercial gas chromatographic instrumentation configured specifically for transformer gas analysis has become available. The newer technology, which makes the analytical task much simpler and more reliable, is described below.

- Column Switching Systems. The two columns necessary for gas separation are connected in a series/by-pass configuration to allow one injection of the extracted gas.

- Detectors. The detectors are mounted in series and the TCD or FID signal selected at appropriate times. Detector and column switching allow one chromatogram to be processed.

- Temperature Programming. The column temperature is increased during the chromatographic run shortening the analysis time, lowering the detection limits, and hastening the elution of heavy molecular weight species which may hold up the injection of the next sample.

- Detection of CO and CO_2. Because CO and CO_2 were traditionally measured by TCD, isothermal analysis was necessary due to the inherent instability of the TCD to temperature and flow rate changes. In the newer gas chromatographs CO and CO_2 are converted to CH_4 in a post-column catalytic converter followed by measurement with an FID detector. The chemical reaction is:

$$CO(CO_2) + H_2 \xrightarrow[Ni]{375°C} CH_4 + H_2O$$

  Using this technique the detection limits for CO and CO_2 are at least 10^3 better than for TCD and due to the relative insensitivity of FID to changes in column temperature, the transformer gases can be run with linear temperature programming.

- Microprocessor Control. Since modern gas chromatographs are microprocessor controlled, injection, valve switching, detector signal switching, detector range changes, and temperature programming are all carried out precisely by the machine. As a result, the analytical data is more precise, less labor-intensive, and the test can be automated.

- Data Reduction Systems. Modern data systems have significantly better data handling and calculation programs. In the present system the gas concentrations are reported with the chromatograms. The data is in its final form and can be transposed directly to the final reporting sheets. Raw chromatographic data is saved and is available should the operator want to examine the machine decisions, intervene and recalculate.

APPENDIX II

RESULTS OF AN ASTM ROUND ROBIN SURVEY

Recently the ASTM conducted a transformer gas round robin survey. The data obtained by a number of participating laboratories on the oil sample are given in Figure II-1. In general, the interlaboratory agreement is poor and some reporting laboratories obtained less than satisfactory precision. In the following discussion the data will be reworked in an attempt to uncover potential problems in the methodology and to determine typical precision of other laboratories.

Some of the most common problems encountered with the analytical system are listed below. These were evident in the round robin data and have been circled in Figure II-1.

1. sampling syringe leaks - these result in a high measured gas content, high O_2 and N_2 content and low results for the other gases

2. vacuum system leaks - these result in a high total gas content, and a high O_2 and N_2 content

3. incomplete gas extraction - incomplete gas extraction results in low and variable gas content measurement

4. calculation mistakes/poor calibration - inaccurate results.

In an attempt to establish a typical "good laboratory" precision outliers (laboratories) in the ASTM data were removed and the data reprocessed. Outliers were removed on the basis of the in-run precision. The relative precision of all laboratories who participated and carried out at least four replicates have been listed in Table II-1.

	H_2	O_2	N_2	CO	CO_2	CH_4	C_2H_6	C_2H_4	C_2H_2	TOTAL
LAB A	1320	8730	57300	430	5450	1570	280	2000	NIL	7.763
	1520	8150	55670	400	5480	1550	310	1980	NIL	7.557
	1620	10050	55710	420	5450	1520	310	2020	NIL	7.765
	1370 (4)	8040	57740	440	5670	1610	340	2180	NIL	7.805
	1210	8050	54450	490	5500	1550	320	2110	NIL	7.427
	1310	7510	52860	420	5120	1370	270	1940	NIL	7.132
	1400	7110	56330	440	5570	1570	330	2120	NIL	7.552
	1310	8220	54960	500	5380	1540	330	1900	NIL	7.468
LAB D	852	9297	52123	550	5295	1258	219	1806	99	7.15
	495	10193	52699	473	5672	1076	197	1608	87	7.15
	907	17383	[82046] (2)	567	5590	1299	230	1874	104	[11.0] (2)
	580	18087	[82459] (2)	511	5154	1164	214	1736	95	[11.0] (2)
	744	9028	50061	529	5164	1194	209	1725	96	6.88
	450	10039	50735	440	4367	989	180	1470	81	6.88
LAB N	[257] (3)	9803	48253	[121] (3)	1250	303	48	446	20	[6.05] (3)
	[463] (3)	11077	44089	[312] (3)	2765	655	121	972	46	[6.05] (3)
	644	12446	52464	474	4164	971	183	1464	70	7.29
LAB J	969	10768	59045	265 ← (1) →	4423	919	156	1422	39	7.87
	816	13417	70246	265	5051	1009	179	1609	43	9.35
LAB F	876	[5240]	[46000]	501	4720	1160	186	1590	94	6.08
	873	[5400] (4)	[46000] (4)	497	4580	1150	185	1550	110	6.08
	993	[5250]	[50200]	570	5530	1330	246	1900	114	6.68
	996	[5350]	[50400]	569	5360	1310	220	1820	110	6.68
LAB C	809	8037	46126	460	3826	1011	135	1246	70	6.17
	813	7755	46023	473	3756	1027	127	1203	70	6.12
LAB G	950	[18000]	49360	530	5620	1410	200	1830	100	7.8
	920	[18300] (4)	50240	530	6320	1360	240	2000	90	8.0
	1000	[18500]	50500	550	5900	1390	220	1850	90	8.0
LAB L	850	10600	52900	500	5270	1180	254	1860	96	7.36
	855	14500	65300	501	5410	1210	219	1860	95	9.0
	815	13400	62000	497	5390	1210	227	1920	97	8.56
	840	[17400] (2)	[78900] (2)	489	5070	1180	214	1840	95	[10.6] (2)
	855	[16900] (2)	[78100] (2)	484	5050	1170	207	1790	95	[10.6] (2)
	855	13700	65300	493	5340	1210	222	1880	95	8.92
MEAN	928	11051	56664	462	4960	1186	221	1721	65	7.76
STD. DEV.	312	4207	10586	96	952	336	65	353	42	1.41
COEFF. VAR. %	34	38	19	21	19	28	29	21	65	18

(1) SYRINGE SAMPLING PROBLEMS

(2) VACUUM LEAK

(3) INSUFFICIENT EXTRACTION

(4) POOR CALIBRATION/CALCULATION ERRORS

FIGURE II-1

DISSOLVED GAS IN OIL ASTM ROUND ROBIN RESULTS

TABLE II-1

PER CENT RELATIVE STANDARD DEVIATION OF REPORTING LABS

Lab	A	B	D	G	L	E	F
n	8	4	6	6	6	4	4
H_2	9	111	28	15	2	20	7
O_2	11	38	34	24	17	10	1
N_2	3	23	26	11	15	4	5
CO	8	108	9	8	1	6	8
CO_2	3	36	9	11	3	7	9
CH_4	5	70	10	6	2	4	8
C_2H_6	8	12	9	12	7	4	4
C_2H_4	5	23	9	5	2	4	10
C_2H_2	-	29	9	10	1	5	8

The data for laboratories B and D were removed and the average gas concentration results for the remaining labs listed in Table II-2.

TABLE II-2

AVERAGE GAS CONCENTRATIONS MEASURED

Gas	Gas Content (μL/L)				
	Lab A	Lab E	Lab F	Lab G	Lab L
H_2	1 382	410	934	872	845
O_2	8 232	5 450	5 310	20 267	14 652
N_2	55 628	33 750	48 150	52 702	67 083
CO	442	310	534	510	494
CO_2	5 452	2 975	5 048	5 498	5 255
CH_4	1 535	715	1 238	1 325	1 193
C_2H_6	311	135	209	223	224
C_2H_4	2 031	1 125	1 715	1 847	1 858
C_2H_2	0	58	107	90	96
T.G.	7.56	4.50	6.38	8.33	9.17

Lab A had an apparent high bias on some gases and low on others and Lab E appears to have made a calculation error of 2X. When the results of Lab E are multiplied by two, a new average can be computed and this has been compared to the average of all labs labelled "overall average" in Table II-3.

TABLE II-3

AVERAGE OF GOOD LAB DATA AND AVERAGE OF ALL LABS

Gas	Good Lab Average (μL/L)	Overall Average (μL/L)
H_2	867	928
O_2	11 825	11 051
N_2	58 212	56 644
CO	520	462
CO_2	5 441	4 960
CH_4	1 344	1 186
C_2H_6	247	221
C_2H_4	1 940	1 721
C_2H_2	103	66
T.G.	8.09	7.76

The overall laboratory average is lower than the "good laboratory" average. This low bias could be attributed to low extraction efficiencies due to the design of the vacuum extraction devices and/or a lack of understanding of the ASTM efficiency factors.

The in-run precision of all 'good' laboratories and the average is listed in Table II-4.

TABLE II-4

ASTM IN-RUN PRECISION

Gas	A	G	L	E	F	Avg Good Lab
H_2	9	15	2	20	7	10.6
O_2	11	24	17	10	1	12.6
N_2	3	11	15	4	5	7.6
CO	8	8	1	6	8	6.2
CO_2	3	11	3	7	9	6.6
CH_4	5	6	2	4	8	5.0
C_2H_6	8	12	7	4	14	9.0
C_2H_4	5	5	2	4	10	5.2
C_2H_2	-	10	1	5	8	4.8

The poorer precision obtained for oxygen and nitrogen is attributed to the gas syringe injection technique used by the majority of the laboratories. In addition, some laboratories may have difficulties in the quantification of hydrogen when large amounts of nitrogen are present in the gas mixture. A negative drift in the baseline of the chromatogram just before elution of H_2 is caused by the adsorption of N_2 into the molecular sieve resulting in a decrease in carrier flow rate. The precision of all other gases are approximately 6-7%.

APPENDIX III

THE ANALYTICAL PROCEDURE

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ANALYTICAL PROCEDURE

METHOD NO:	
REVISION NO:	
REVISED:	
ORIGINAL METHOD NO:	
METHOD TYPE:	
FILE NO:	
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TITLE: ANALYSIS OF DISSOLVED GASES IN TRANSFORMER OILS BY VACUUM EXTRACTION GAS CHROMATOGRAPHY

R.E. Massey REM 15/11/85

REVISIONS: BRIEF DESCRIPTION AND REASON	PAGE	PARAGRAPH	DATE

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DISTRIBUTION: *All Analytical Services Technicians*

I. Hunter (Senior Technician)

W. Schmidt (Technician)

ANALYTICAL PROCEDURE CHECK LIST

METHOD NO: .

REVISION NO:

TITLE: ANALYSIS OF DISSOLVED GASES IN TRANSFORMER OILS BY VACUUM EXTRACTION GAS CHROMATOGRAPHY

EQUIPMENT & SUPPLIES:

- Gas Chromatograph with FID and TCD Detectors
- Poropak N and Molecular Sieve 13X columns
- Gas sampling valve
- Vacuum extraction system for sample preparation

STANDARDIZATION:

Two standard gas mixtures containing H_2, O_2, N_2, CH_4, CO, CO_2, C_2H_4, C_2H_6 and C_2H_2 are available. The GC is calibrated with either one of these mixtures using an external calibration routine and single point linear calibration. Standards are run with each days samples.

1.0 OUTLINE OF THE METHOD

The detection of certain gases generated in an oil-filled transformer is frequently the first available indication of a possible malfunction that may eventually lead to failure. Normal operation of a transformer leads to the formation of some gases and the dissolution of air. When faults occur in the transformer such as arcing, corona discharge, low energy sparking, severe overloading and overheating in the insulation system, the oil or insulation material decomposes. The type of fault may be determined by the kinds of gases generated. The extent of the fault may be determined by the rate of generation of gases with time. Severe faults are usually detected in the field and then confirmed by GC analysis. Incipient faults are detected with the comparison of operational and gas analysis data collected over the years with a sampling periodicity of approximately one year. A description of criterion used to evaluate analysis results can be found in 4.1 and 4.2.

In a transformer, generated gases will be found dissolved in the insulating oil. They may also be found in the gas blanket above the oil or in gas collecting devices (gas-relay).

The analytical method described here covers the measurement of gases dissolved in electrical insulating oil (Voltesso 35).

The individual component gases that may be identified and determined include.

Hydrogen	- H_2
Oxygen	- O_2
Nitrogen	- N_2
Methane	- CH_4
Carbon Monoxide	- CO
Carbon Dioxide	- CO_2
Ethylene	- C_2H_4
Ethane	- C_2H_6
Acetylene	- C_2H_2

2.0 CONCENTRATION RANGE

Transformer oil samples can be divided into two categories, typical oils with normal gas contents and faulted oils containing significantly higher amounts of gas. The expected concentration ranges for both sample types are listed in Table 1. Typical oils are analyzed with a method called TRANS and faulted oils with a method called TRANS HI. For comparison, the MDQ and upper limits are listed for TRANS and TRANS HI in the Table.

TABLE 1. Sample Type and Method Application

Gas	Gas Content µL/L			
	Typical Oils		Faulted Oils	
	Expected Range	TRANS Range	Expected Range	TRANS HI Range
H_2	5-800	5-600	<50-6 000	125-15 000
O_2	300-25 000	100-40 000	300-25 000	200-100 000
N_2	17 000-90 000	100-150 000	17 000-90 000	250-375 000
CH_4	8-280	2-1 000	200-35 000	50-25 000
CO	80-1 000	20-1 200	<20-2 000	500-7 500
CO_2	200-4 000	20-5 000	1 000-10 000	500-15 000
C_2H_4	1-1 000	2-3 000	500-85 000	50-20 000
C_2H_6	2-200	2-400	500-18 000	50-17 500
C_2H_2	2-300	2-200	<2-34 000	50-5 000

3.0 PRECISION

The precision of the test has been estimated using replicate measurements of an oil sample from transformer T13 at Manby TS. The relative standard deviation data is listed in Table 2. Each "set" of data represents the in-run relative standard deviation computed for the analysis of five samples of oil. The elapsed time between sets was one month. In total the data represents the analysis of 30 syringes and 30 analyses. The expected precision is 5% or better for oils with similar concentrations of gases.

TABLE 2. In-Run Precision

Gas	Level µL/L	Relative Standard Deviation						
		Set 1	Set 2	Set 3	Set 4	Set 5	Set 6	AVERAGE
H_2	45	3.9	6.16	4.33	4.93	2.84	5.16	4.55
O_2	25 000	3.3	1.89	3.11	(8.26)	(9.12)	1.13	2.36
N_2	67 000	0.53	0.708	1.55	(8.08)	(6.36)	0.724	0.878
CH_4	20	0.94	0.737	1.25	1.04	0.839	0.858	0.944
CO	300	1.3	2.98	1.01	2.20	3.66	0.726	1.98
CO_2	2 400	4.9	4.41	0.829	2.13	(12.6)	1.11	2.68
C_2H_4	35	1.5	1.67	1.85	2.33	3.90	1.61	2.14
C_2H_6	11	1.4	1.37	3.72	2.73	1.37	3.45	2.34
C_2H_2	55	2.4	1.56	6.69	2.36	4.29	3.50	3.47
Total Gas	90 000	1.0	0.685	1.24	(5.98)	(6.30)	0.768	0.923

+ numbers in brackets not included in average

The day-to-day precision has been measured for the same T13 Manby TS sample. The results for two sets of 20 analyses carried out on 20 consecutive working days were compiled and the average and relative standard deviation computed. These results are listed in TABLE 3.

TABLE 3. Day-To-Day Precision

Gas	Level µL/L	Relative Standard Deviation		
		Set 1	Set 2	Average
H_2	45	4.15	5.61	4.88
O_2	25 000	0.106	0.779	0.443
N_2	67 000	2.57	4.96	3.77
CH_4	20	3.15	3.15	3.15
CO	300	3.70	5.21	4.46
CO_2	2 400	2.69	2.43	2.56
C_2H_4	35	4.33	9.33	6.83
C_2H_6	11	7.91	5.22	6.57
C_2H_2	55	5.26	5.59	5.43
Total Gas	90 000	2.70	4.88	3.79

4.0 REFERENCES

4.1 IEEE Guide for the Detection and Determination of Generated Gases in Oil-Immersed Transformers and their Relation to the Serviceability of the Equipment. ANSI/IEEE C57.104-1978.

4.2 Interpretation of the analysis of gases in transformers and other oil-filled electrical equipment in service. IEC Publication 599, 1978.

4.3 Guide for the sampling of gases and of oil from oil-filled electrical equipment and for the analysis of free and dissolved gases. IEC Standard, Publication 567, 1977.

4.4 Standard Methods of Sampling Electrical Insulating Oils for Gas Analysis. ASTM, D3613, 1982.

4.5 Transformer Oil and Gas Sampling. Technical Procedure Hydraulic Generation & Transmission Functions, Ontario Hydro HO363, November 1981.

4.6 Standard Method for Analysis of Gases Dissolved in Electrical Insulating Oil by Gas Chromatography. ASTM D3612 1979.

4.7 B. Thompson, Analysis of Gases in Transformer Fluids, Varian Instruments at Work, Number 49, March 6, 1981.

4.8 B. Thompson & R. Wood, The Methanizer in the Model 3700 and Vista Series Gas Chromatographs, Varian Instruments at Work, Number 54, July 31, 1981.

4.9 VISTA 401 OPERATORS GUIDE, Varian Associates, Inc. 1981 Publication Number 03-913909-00, May 1981.

4.10 VISTA 6000 GAS CHROMATOGRAPHY OPERATORS MANUAL, Varian Associates, Inc. Publication Number 03-913855-00, June 1981.

5.0 COLLECTION AND STORAGE OF SAMPLES

5.1 Transformer Oil

Transformer oil samples are taken from the sampling tap on the bottom of the transformer. A glass syringe fitted with a 3-way valve is attached to the tap with a small piece of plastic tubing. Oil is allowed to flow through the tubing and the valve to remove air and then the valve is operated to flush the syringe. A 30 mL oil sample is taken and the syringe is placed in a cardboard box for shipment to the Kipling laboratory. A complete description of the sampling operation can be found in References 4.3, 4.4, and 4.5.

Some important sampling and storage aspects which must be considered are listed below.

Dissolved Oxygen - Some of the dissolved oxygen present in the oil sample may be consumed by oxidation. The reaction can be delayed by exclusion of light, ie, store the syringes in cardboard boxes provided.

Gas-Tight Syringe - The gas tightness of a syringe may be tested by storing an oil sample in a syringe for two weeks and analyzing aliquots for hydrogen at the beginning and at the end of this period. An acceptable syringe will permit losses of less than 2.5% each week.

Degassing - Oil samples may, on contraction, release bubbles of gas. This loss will change the composition of the dissolved gases. The magnitude of the error will depend on the size of

of the bubble in relation to the volume of the oil sample and on the solubility of the gas.

Storage Time - Samples should be analyzed within two weeks of sampling due to the possibility of decomposition. In addition, due to the magnitude of the monitoring program, syringes must be put back into circulation as soon as possible.

Wetting of Glass Surfaces - A cleaned glass surface is difficult to wet with mineral oil, and as a result minute gas bubbles can be entrained on the surface. These cause inhomogeneity of the sample with respect to O_2 and N_2 especially on samples with low O_2 content. Syringes must be flushed with new transformer oil before they are returned to the field.

6.0 GAS STANDARDS

Two gas standards are available, one for typical transformer samples and the method "TRANS" and one for faulted samples (TRANS HI). The gas component concentrations in these primary standards are listed below:

Gas	Gas Concentration (µL/L)	
	TRANS	TRANS HI
H_2	1 492 ± 15	14 900 ± 150
O_2	199 100 ± 200	30 300 ± 200
N_2	769 572 ± 1000	551 000 ± 299
CH_4	497 ± 5	49 600 ± 200
CO	5 960 ± 60	14 900 ± 150
CO_2	19 900 ± 200	40 100 ± 200
C_2H_4	497 ± 5	49 700 ± 200
C_2H_6	497 ± 5	49 500 ± 200
C_2H_2	497 ± 5	9 940 ± 100
C_3's	present	-
C_4's	present	-

Five hundred microlitres of gas standards are taken with a 1 mL glass syringe for calibration of the instrument.

7.0 APPARATUS

7.1	Sampling Syringes	Hypodermic Syringe 30 cc Glass Luer Tip, Graduated: 1cc Hydro Stores Catalogue
7.2	3-Way Valves (Stopcock)	K75 American Hospital Supply 1076 Lakeshore Blvd Mississauga, 821-9660
7.3	Gas Chromatograph	Varian 6000 Series Microprocessor controlled. GC with a gas sampling and column switching system, nickel catalyst and TCD and FID detectors.
7.4	A 10' x 1/8" column p/w Molecular Sieve 13 x 45/60 mesh	Batch No R20924 Supelco Canada Ltd
7.5	A 12' x 1/8" SS column p/w Poropak N 50/80 mesh	Batch No R20805 Supelco Canada Ltd
7.6	Data System	Varian Vista 402 with dual floppy discs.
7.7	Vacuum System	The vacuum system is described in Section 8.1.2. This system resembles the ASTM Vac system and includes gas extraction flask and a Toepler pump. Instead of septa and a gas buret, a GSV is interfaced to the vacuum system.
7.8	Gas Tight Syringes	Hamilton 1 mL # 1001
7.9	ARGON (Zero Gas)	Wetmore Welding (1A)
7.10	Air (Zero Gas)	Wetmore Welding (1A)
7.11	Hydrogen (Zero Gas)	Wetmore Welding (1A)

7.12 Air (prepurified) — Wetmore Welding (1A)

7.13 Top Loading Balance.

7.14 Analytical Gas Standards — Matheson Canada Ltd. see Section 6.0

8.0 PROCEDURE

8.1 Instrumental Set-Up

8.1.1 Operation of the Vista GC. - The instructions and descriptions that follow assume that the operator is proficient in the operation of a gas chromatograph and an electronic integrator. The specific instructions for the Varian 6000 GC and the Vista 402 data station can be found in the operating manuals (see References 4.9 and 4.10). Two separate methods are described below, one method called TRANS and another TRANS HI.

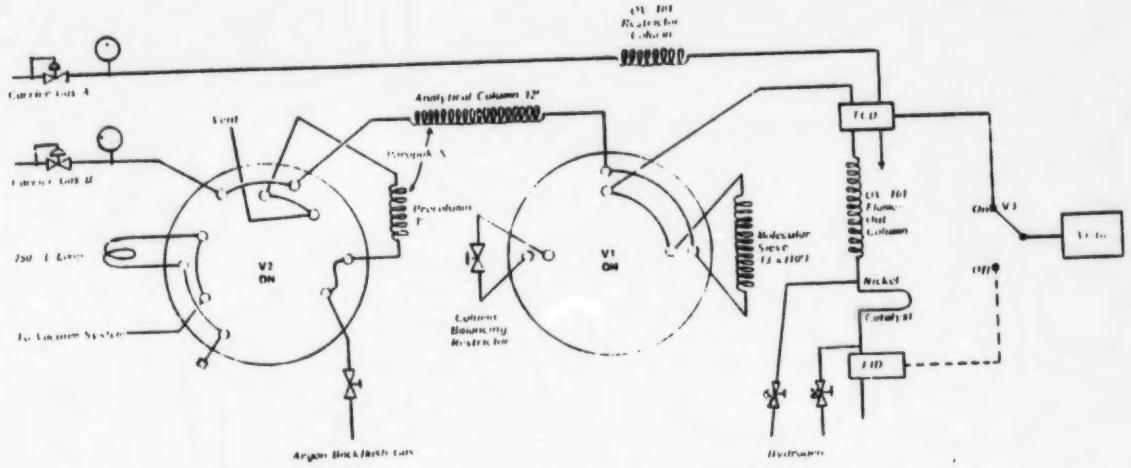
A schematic diagram of the GC valving and detector system is shown in Figure 1. There are four hardware changes made during the chromatographic run.

Configuration 1 — The sample is loaded into the gas sampling loop.

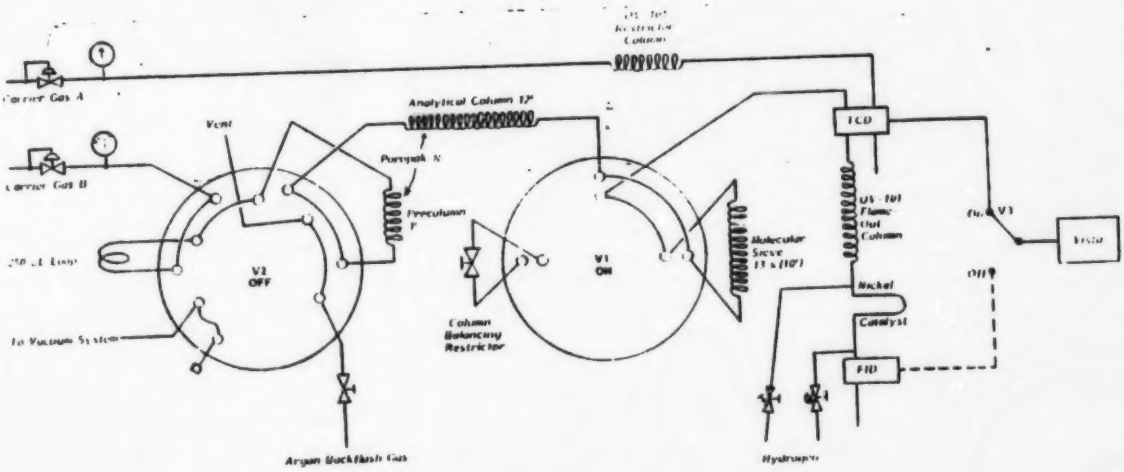
Configuration 2 — The sample is injected into the gas chromatograph including 1' + 12' Poropak + 5-1/2' Molecular Sieve columns in series. The signal monitored is from the TCD detector and H_2, O_2 and N_2 are measured.

Configuration 3 — The 10 port valve rotates back into its initial position. Heavier hydrocarbons C-3, C-4, C-5 are backflushed to vent. The detector signal is switched to FID to monitor CH_4 and CO from the molecular sieve column.

Configuration 4 — The 6 port valve rotates to bypass the molecular sieve column and CO_2, C_2H_4, C_2H_6 and C_2H_2 are monitored off the Poropak N column by FID.

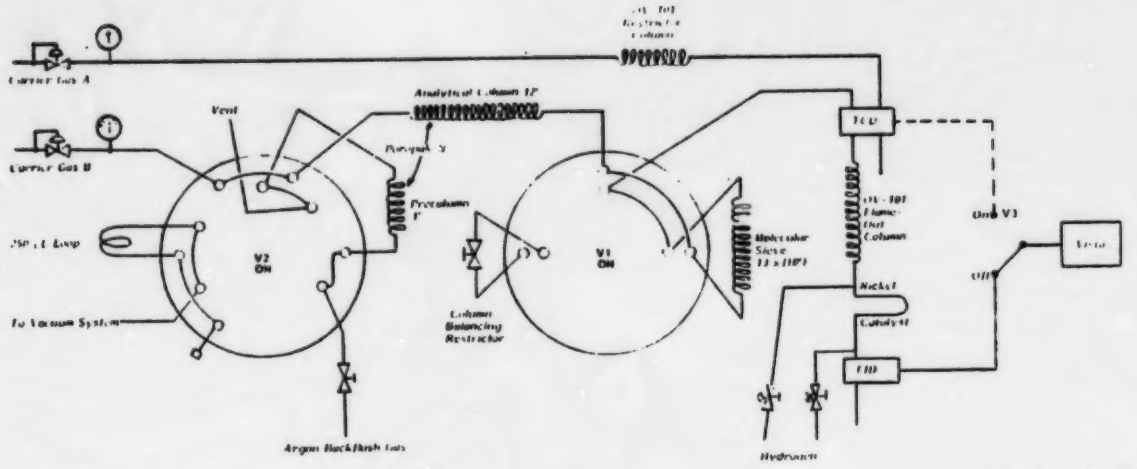


CONFIGURATION 1
INITIAL CONDITIONS
(T = 0.00 min)



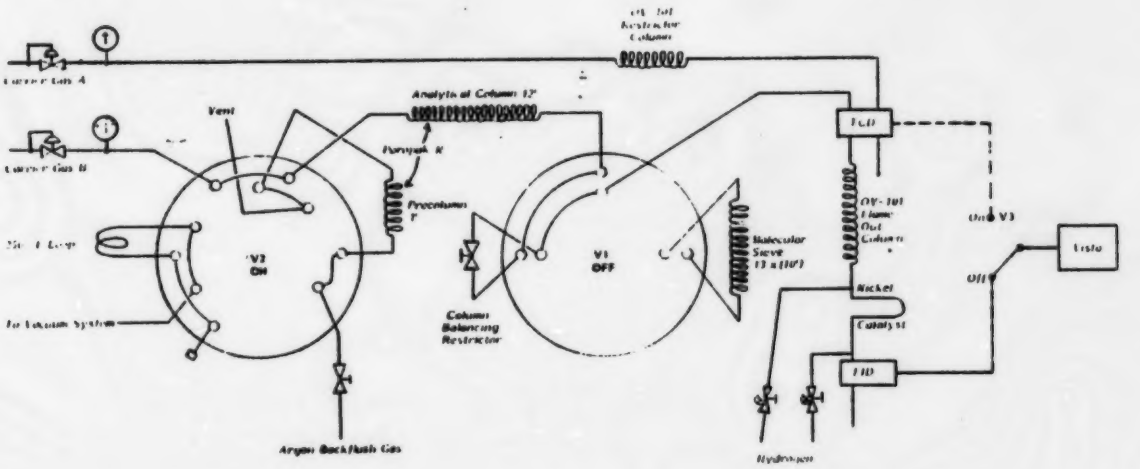
CONFIGURATION 2
SAMPLE INJECTION
(T = 0.01 min)

FIGURE 1
TRANSFORMER GAS VALVING AND DETECTOR CONFIGURATION



CONFIGURATION 3

PRECOLUMN BACKFLUSH TO VENT SWITCH TO FID
(T = 4.20 min)



CONFIGURATION 4

MOLECULAR SIEVE BY-PASS
(T = 6.40 min)

The two procedures TRANS and TRANS HI which must be programmed into the Vista 402 are listed below.

SINGLE CHANNEL METHOD: TRANS

```
SECTION 1:  BASIC
PAGE 1
   ANALYSIS PARAMETERS
   CHANNEL:  1
   CALCULATION:  ES
   AREA/HT:  A
   STOP TIME:  11.50
   NUMB EXPECTED PKS:  500
   EQUILIBRATION TIME:  0
   UNRETAINED PK TIME:  0.00
   UNIDENT PK FACTOR:  0.000000
   SLICE WIDTH:  10

PAGE 2
   SAMPLE PARAMETERS
   RUN TYPE:  A
   SAMPLE ID:  TRANS GAS
   DIVISOR:  wt of oil
   AMT STD:  0.56870
   MLTPLR:  0.86

PAGE 3
   REPORT INSTRUCTIONS
   WHERE TO REPORT:  L
   COPIES:  1
   TITLE:  TRANSFORMER GAS ANALYSIS
   FORMAT:  N
   DECIMAL PLACE:  4
   RESULT UNITS:  UL/L
   REPORT UNIDENT PKS:  N
   REPORT INSTRUMENT CONDITIONS: N

PAGE 4
   PLOT INSTRUCTIONS
   PLOT:  Y
   ZERO OFFSET:  5
   ANNOTATION
      RETENTION TIME:  Y
      PLOT CONTROL:  Y
      TIME TICKS:  Y
      TIME EVENTS:  N
      PK START/END:  Y
```

PAGE 5
CHART SPEED
PAGES OR CM/MIN: C
INIT VALUE: 1.0

PAGE 6
PLOT ATTEN
INIT PLOT ATTEN: 64

LINE#	TIME	PLOT ATTEN
1	0.10	1024
2	1.80	32
3	3.00	256
4	5.50	32

SECTION 2: TIME EVENTS
PAGE 1

LINE#	TIME	EVENT	VALUE
1	0.00	PR	100
2	0.00	SN	2
3	0.00	T%	5.0
4	0.00	WI	4
5	2.38	II	2.39
6	2.85	II	2.86
7	3.17	II	3.18
8	4.98	T%	4.99
9	5.90	II	5.91
10	8.44	T%	80.0
11	10.35	II	10.36
12	10.75	II	10.76
13	11.40	II	11.41

SECTION 3: PEAK TABLE
PAGE 1
STD PK#: 0
RELATIVE RETEN PK#: 3
RESOLUTION PK#: 0
RESOLUTION MINIMUM: 0.0
FACT%: 10.0
IDENTIFICATION TIME WINDOWS +/-
REF
%: 4
MIN: 0.00
NON REF
%: 5
MIN: 0.00

PAGE 2

PK#	TIME	NAME	FACTOR	AMOUNT	REF	GR#	MUST LO	MUST HI
1	2.58	*H2-------	277.5140	1492.000			5.000000	600.0000
2	3.41	*O2-------	2781.990	199100.0			300.0000	40000.00
3	4.02	*N2-------	3526.980	769572.0	R		300.0000	150000.0
4	6.14	*CH4------	62.18650	497.0000			2.000000	300.0000
5	6.90	*CO-------	53.93490	5960.000			20.00000	1200.000
6	8.49	*CO2------	60.83990	19900.00			20.00000	4000.000
7	9.48	*C2H4-----	26.14870	497.0000			2.000000	200.0000
8	10.12	*C2H6-----	25.52530	497.0000			2.000000	200.0000
9	11.05	*C2H2-----	29.14220	497.0000			2.000000	200.0000

SECTION 4: GC INSTRUMENT CONTROL

PAGE 1

COL TEMP

ISO/INIT COL TEMP: 50

INIT HOLD TIME: 5.50

STEP#	FINAL TEMP	RATE	HOLD TIME
1	170	20.0	1.00

PAGE 2

DETECTORS

DET A TYPE: FID

DET B TYPE: TCD

LN#	TIME	SIDE	ATTN	RANGE	ZERO
1	0.00	A	32	11	Y
2	0.00	B	128	.05	Y
3	1.80	B	128	.05	Y
4	5.00	A	64	11	Y

PAGE 3

TEMP/FLOW

INJ A TEMP: 375

INJ B TEMP: 100

ION TEMP: 300

TCD TEMP: 135

TCD FIL TEMP: 220

AUX TEMP:

COL A FLOW: 24

COL B FLOW: 23

PAGE 4

LN#	TIME	RELAY ON	RELAY OFF
1	0.00	123	
2	0.01	13	2
3	5.00	2	3
4	7.90		1

```
SECTION 7:  POST RUN
PAGE 1
   FILE NAME:  TRANS
   SAVE INSTRUCTIONS
      TYPE:  RAW
      WHERE TO SAVE:  U
   TRANSMIT/REPLOT INSTRUCTIONS
      TRANSMIT RAW DATA: N
      REPLOT WITH BASELINES:  N
      RAW DATA LOCATION:  U
      TRANSMIT REPORT:  N

PAGE 2
   METHOD LINKING INSTRUCTIONS
      METHOD:
      LINK CALC RESULTS:  N
   PROGRAM EXECUTION
      PROGRAM:
      PARAMETERS:
      RESERVE PRINTER: Y

SECTION 10:  NOTE PAD
PAGE 1
      LINE#              VALUE
      1       REPORT#--------------TRANS#---------SYRINGE#
      2
      3       LOCATION------------SAMPL DATE ----OPER POSITION
      4
      5       BUBBLE Y N-----------COLOR L M D --- SAMPL POINT
```

SINGLE CHANNEL METHOD: TRANS HI

```
SECTION 1:  BASIC
PAGE 1
   ANALYSIS PARAMETERS
   CHANNEL:  1
   CALCULATION:  ES
   AREA/HT:  A
   STOP TIME:  11.50
   NUMB EXPECTED PKS:  500
   EQUILIBRATION TIME:  0
   UNRETAINED PK TIME:  0.00
   UNIDENT PK FACTOR:  0.000000
   SLICE WIDTH:  10
```

```
PAGE 2
   SAMPLE PARAMETERS
   RUN TYPE:  A
   SAMPLE ID:  TRANS HI GAS
   DIVISOR:  wt oil
   AMT STD:  0.500
   MLTPLR:  0.86

PAGE 3
   REPORT INSTRUCTIONS
   WHERE TO REPORT:  L
   COPIES:  1
   TITLE:  TRANSFORMER GAS ANALYSIS
   FORMAT:  N
   DECIMAL PLACE:  4
   RESULT UNITS:  UL/L
   REPORT UNIDENT PKS:  N
   REPORT INSTRUMENT CONDITIONS: N

PAGE 4
   PLOT INSTRUCTIONS
   PLOT:  Y
   ZERO OFFSET:  5
   ANNOTATION
      RETENTION TIME:  Y
      PLOT CONTROL:  Y
      TIME TICKS:  Y
      TIME EVENTS:  N
      PK START/END:  Y

PAGE 5
   CHART SPEED
      PAGES OR CM/MIN:  C
      INIT VALUE:  1.0

PAGE 6
   PLOT ATTEN
      INIT PLOT ATTEN:  64
   LINE#  TIME  PLOT ATTEN
   1      0.01     1024
   2      2.00     8
   3      5.00     64
```

SECTION 2: TIME EVENTS
PAGE 1

LINE#	TIME	EVENT	VALUE
1	0.00	PR	100
2	0.00	SN	2
3	0.00	T%	5.0
4	0.00	WI	4
5	2.33	II	2.34
6	7.70	II	7.71
7	8.90	II	8.91
8	10.45	II	10.46
9	11.40	II	11.41

SECTION 3: PEAK TABLE
PAGE 1

STD PK#: 0
RELATIVE RETEN PK#: 3
RESOLUTION PK#: 0
RESOLUTION MINIMUM: 0.0
FACT%: 15.0
IDENTIFICATION TIME WINDOWS +/-
REF
%: 4
MIN: 0.00
NON REF
%: 5
MIN: 0.00

PAGE 2

PK#	TIME	NAME	FACTOR	AMOUNT	REF	GR#	MUST LO	MUST HI
1	2.56	*H2-------	5739.600	14900.00			125.0000	15000.00
2	3.41	*O2-------	58269.20	30300.00			300.0000	100000.0
3	4.03	*N2-------	68773.60	551000.0	R		300.0000	375000.0
4	6.12	*CH4------	1175.590	49600.00			50.00000	25000.00
5	6.90	*CO-------	1031.100	14900.00			500.0000	7500.000
6	8.51	*CO2------	1169.250	40100.00			500.0000	15000.00
7	9.50	*C2H4-----	525.4270	49700.00			50.00000	20000.00
8	10.13	*C2H6-----	524.1120	49500.00			50.00000	17500.00
9	11.08	*C2H2-----	820.9090	9940.000			50.00000	5000.000

SECTION 4: GC INSTRUMENT CONTROL
PAGE 1

COL TEMP
ISO/INIT COL TEMP: 50
INIT HOLD TIME: 5.50

STEP#	FINAL TEMP	RATE	HOLD TIME
1	170	20.0	0.5

PAGE 2

DETECTORS

DET A TYPE: FID

DET B TYPE: TCD

LN#	TIME	SIDE	ATTN	RANGE	ZERO
1	0.00	A	32	10	Y
2	0.00	B	128	.5	Y
3	1.80	B	128	.5	Y
4	5.20	A	64	10	Y

PAGE 3

TEMP/FLOW

INJ A TEMP: 375

INJ B TEMP: 100

ION TEMP: 300

TCD TEMP: 135

TCD FIL TEMP: 220

AUX TEMP:

COL A FLOW: 24

COL B FLOW: 23

PAGE 4

LN#	TIME	RELAY ON	RELAY OFF
1	0.00	123	
2	0.01	13	2
3	5.20	2	3
4	8.00		1

SECTION 7: POST RUN

PAGE 1

FILE NAME: TRANS HI

SAVE INSTRUCTIONS

TYPE: RAW

WHERE TO SAVE: U

TRANSMIT/REPLOT INSTRUCTIONS

TRANSMIT RAW DATA: N

REPLOT WITH BASELINES: N

RAW DATA LOCATION: U

TRANSMIT REPORT: N

PAGE 2

METHOD LINKING INSTRUCTIONS

METHOD:

LINK CALC RESULTS: N

PROGRAM EXECUTION

PROGRAM:

PARAMETERS:

RESERVE PRINTER: Y

SECTION 10: NOTE PAD
PAGE 1

LINE#	VALUE
1	REPORT#----------TRANS#---------SYRINGE#
2	
3	LOCATION----------SAMPL DATE ----OPER POSITION
4	
5	BUBBLE Y N----------COLOR L M D

8.1.2 Operation of the Vacuum System - A schematic diagram of the vacuum system is shown in Figure 2. The function of this system is twofold: 1) to provide a large volume at low pressure into which dissolved gases will be efficiently extracted from oil and 2) to provide a means of compressing a gas into a gas sampling valve. The following procedure is applicable for the handling of aliquots of the standard gas and gas extracted from oil. The specific extraction procedure for oil will be described in Section 8.1.4.

a) Evacuate the vacuum system with valves V1, V2, V4, V5, and one of either SV1 or SV2 open. Monitor the vacuum on the Pirani gauge and allow evacuation to $<2x10^{-3}$ Torr. Close V1 and observe the vacuum reading. Make sure there is no gross leaks.

An acceptable leak rate is equivalent to a vacuum change of $<5x10^{-4}$ Torr/min. If the leak is greater than this the problem area must be located and rectified.

b) Inject either the gas standard or an oil sample by way of the septa on the sampling flask.

c) Close V2, rotate V3 to allow air to enter the bottom compartment of the Toepler pump. Allow the level of Hg to rise above V4 then close V4.

Caution: Do not allow the Hg to rise rapidly. The force of the Hg on the tubing above the Toepler may be enough to shatter the glass.

d) Rotate V3 to evacuate the bottom chamber of the Toepler pump. When the Hg level falls below V2 open V2. Continue evacuation until the level of Hg in the Toepler pump comes to rest. Then Close V3.

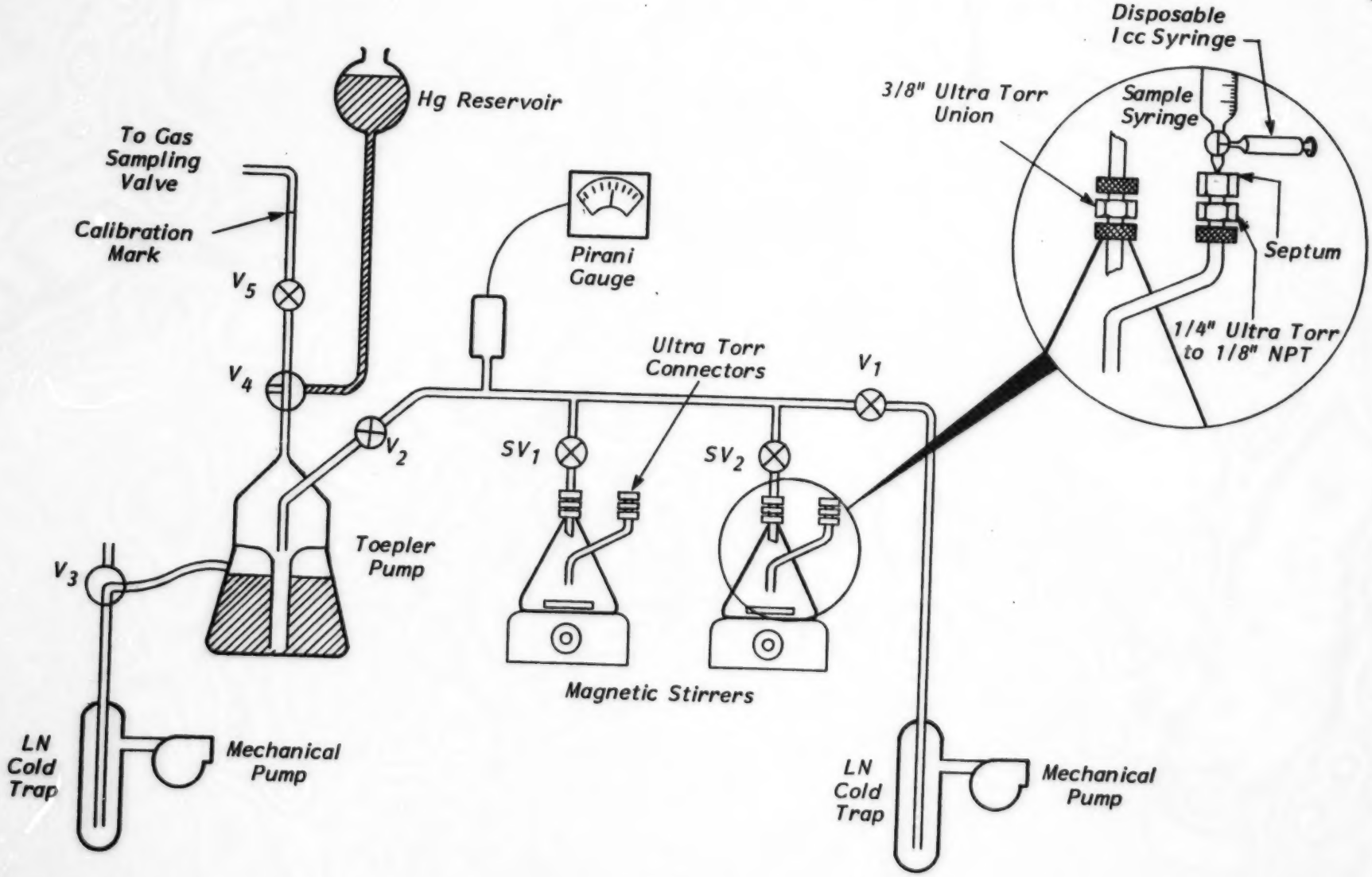


FIGURE 2
THE VACUUM SYSTEM

e) Wait one minute then close V2, rotate V3 to allow air to enter the bottom of the Toepler pump. When the Hg level has risen about 1/2 way open V4. Allow Hg to rise above V4 and then close V4.

The small amount of Hg trapped above V4 will drop into the main Hg reservoir.

f) Rotate V4 to connect the Hg reservoir with the upper portion of the Toepler and to compress the gas further and allow the Hg level to rise to the calibration mark. Close V5.

The gas sample is now loaded into the GSV and ready for injection into the GC.

g) Rotate V4. Bring the Hg down by rotating V3. When the Hg level falls below V2 open V2, close SV1 and open V1.

If a gas standard has been run there is no need to remove the sampling flask. If an oil was run, the flask can be removed at this point and the oil drained.

h) After the sample is injected into the GC, open V5. Evacuate the system. Open SV2 to evacuate the the second sampling flask.

4.2 min into the run when the 10 port GSV returns to load, 750 µL of argon is injected into the vacuum system. You must wait for this before attempting to inject another sample.

8.2 Analysis

8.2.1 Sample Registration and Management - When a sample is received the following information must follow the sample and be recorded with all analytical results.

transformer sampling point, station
transformer serial number, make
syringe number
sampling date.
operating position

When the samples are transferred to the laboratory each syringe is given a number which runs consecutively from 1 to 3000 and this number is listed along with the above information on the "TGA Analysis Schedule" shown in Figure 3. With the transformer serial number the historical analytical data can be obtained.

TGA Analysis Schedule

Analysis Date	*Lab Number*	*Syringe Number*	*Station*	*Transformer Serial Nbr.*	*Report Number*	*Rack / Vial*	*Comments*

FIGURE 3

TGA ANALYSIS SCHEDULE

The historical data is used to aid in the evaluation of results with respect to accuracy and to determine whether a serious problem exists which requires immediate attention.

8.2.2 Calibration of the GC - The gas chromatograph is calibrated by injecting a known quantity of the gas standard into the vacuum system, compressing this gas into the gas sampling valve as described in Section 8.1.2., and injecting this sample into the GC. Prior to a calibration run the method TRANS or TRANS HI must be modified by changing the run type from "A" (analysis) to "C" (calibration). This modification allows the data system to use peak areas and the amount of gas specified by the user to calculate calibration factors.

The calculation technique used by the Vista 402 is an external standard single point calibration. The calibration factors are calculated using the following equation:

$$\text{FACTOR}_i = \frac{\text{Gas Std Conc}_1 \times \text{Vol Std Inj}}{\text{AREA STD}_i} \times 10{,}000$$

where

Factor_i = calibration factor for gas component i

Gas Std Conc_i = conc of gas component i in the primary standard

Vol Std Inj = mL of standard gas injected into the vacuum system

= "AMT STD" Section 1; Page 2 of the method

AREA STD_i = Peak area of gas component i measured by GC

10,000 = scaling factor.

When the gas standard has been run, a calibration report is printed with all calibration factors calculated. These new factors have been compared to any previous factors which are stored in memory and if the new factor meets a pre-set criterion (±15%) the data system prints a "U" after the calibration factor which means the new factor meets the criterion and has been weighted

and averaged with previous calibration factors to produce the working "FACTOR". If no "U" follows the calibration factor one must investigate (ie, loss in detector sensitivity, poisoned methanizer, incorrect injection, failed vacuum system).

When the calibration is finished the GC method must be modified by replacing "C" with "A" in Section 1; Page 2; line 2. This directs the data system to treat subsequent injections as unknowns and calculates concentrations. The calculation is discussed in Section 8.2.4.

8.2.3 Running an oil sample.

a) Remove syringe from cardboard box. Check the syringe number with the data on the field sampling sheet and the lab number on the work scheduling sheet.

b) Weigh the syringe and 3-way valve on a top loading balance and record the weight.

c) Attach the Luer fitting of the valve to a 21G1-1/2 needle, attach a 1 cc syringe to the side port and penetrate septum of the sampling flask.

Becton Dickson No 5169

d) Open the sampling flask valve and evacuate the sampling flask and 3-way valve.

e) Introduce the oil sample by rotating the 3-way valve stem down and allow 5 mL of oil to drain into the sampling flask. Close the 3-way valve (Stem 90° to the syringe).

f) Turn on the magnetic stirrer and stir the oil vigorously for 10 min.

g) Compress the gas into the GSV as described in 8.1.2c to 8.1.2g.

h) Close SV1. Disconnect the syringe from the needle tip, remove the 1 cc disposable syringe and reweigh the sample.

With SV1 closed the flow of air through the needle tip is slow enough to safely repressurize the sampling flask before it can be removed.

i) Calculate the sample weight and modify the method in Section 1: Page 2 DIVISOR and MULTIPLIER

j) Inject the sample into the GC.

8.2.4 Calculation - After the unknown sample has been run the chromatographic peaks are identified and the peak area measured (A_i). The Vista then uses the following equation to compute the gas content:

$$\text{Gas Concentration}_i = \frac{A_i \times \text{FACTOR}_i}{\text{DIVISOR} \times 10{,}000} \times \text{MLTPLR}$$

where: $\text{Gas Concentration}_i$ = conc in μL/L of gas component i
A_i = peak area measured for gas i
DIVISOR = wt spl (SECTION 1, PAGE 2) of method
MLTPLR = 0.86 (the density of Voltesso oil).

The total dissolved gas is computed by the Vista as it sums the component gas concentrations $\sum_{i=1}^{10} (\text{Gas Concentration}_i)$. This number is reported under TOTALS and must be divided by 1000 to convert to mL/L as required by the client or by 10,000 to convert to % (vol).

8.3 Reporting

Transfer Vista data directly onto the computer reporting sheet. Check that the serial number and all other data are correct. If the data indicates a significant increase in individual gas components the analytical results should be reported immediately to J. Salovarra, Hyd Gen & Tran, U10E01, 2+4413. Otherwise the

report is processed in the normal manner and sent to the client by mail.

In addition to reporting the results of unknown transformer oil samples, each computer sheet should also have data obtained for the quality assurance sample. This indicates to the client that we have taken care to monitor the quality of the analytical service on a daily basis.

8.4 Quality Assurance

A control sample must be run each day with regular transformer oil samples. This sample is obtained from T13 at Manby TS. Six syringes filled with this sample are obtained by calling B. Yew (Ext 6473). Upon receipt of these syringes a subsample of each syringe is analyzed and an average for each gas computed. This average is then taken as the expected concentration.

Each day one syringe must be selected and analyzed as an unknown and the data documented on QA sheets. Calculate the ratio of expected versus found. This ratio should be within 0.9 to 1.1. If the ratio is not within this range then the analyst must determine the cause and correct the problem. If the results for the QA sample are out of specification the rest of the results may or may not be reported. This is at the discretion of the senior technician.

Some examples of problems encountered over two year are listed below.

Symptoms	Probable Cause
High N_2, high O_2, high total gas	vacuum leak
High CH_4 or no CH_4	molecular sieve column requires reactivation
Low CO_2, tailing peak	methanizer poisoned, replace
All gases high	incorrect "DIVISOR"
All gases low	incorrect "DIVISOR"
O_2 low	chemical or photochem degradation of the sample
High C_2H_4, C_2H_6	Vac system interferences after Vac system cleaning
Low H_2	leakage of gas from the syringe
High H_2	incorrect peak start
High C_2H_4, C_2H_6, C_2H_2	Poropak N bleeding incorrect baseline used.